8.0 QUALITY ASSURANCE/QUALITY CONTROL

8.1 QUALITY ASSURANCE:

A set of operating principles that, if strictly followed during sample collection and analysis, will produce data of known and defensible quality. That is, the accuracy of the analytical result can be stated with a high level of confidence.

8.1.1 Chemicals/Reagents/Gases:

Ultra Pure chemicals and Ultra High Purity gases or better will be used for all metals analyses. Standards will be supplied with a Certificate of Analysis showing Manufacturer's number, Description, Lot number, Expiration date, Labeled and Measured values and Traceability to NIST SRM's. Individual analytical approved methods may specify additional requirements for the reagents to be used. All reagents will be logged and dated as to the date received and date opened with the analysts= initials, follow all SOP's forchemical receiving. No chemical/reagent will be used past its expiration date. All expired reagents will be disposed of in the proper manner.

8.1.2 Contamination:

The detection limits attainable with the Plasma II are often a function of the amount of contamination present, rather than instrumental capabilities. The following precautions contribute to avoid inorganic contaminants.

General and customary **safety practices as well as those included in instrument manufacturer's manuals and approved methods will be strictly followed. Material Safety Data Sheets will be consulted before using any new or unknown chemical/reagent.

****Glassware preparation**: All glassware used for metals analyses will be separate from all other in the Lab and be specified as such. Only Class A Volumetric glassware will be used. All glassware will be cleaned according to the following procedure:

Between sample transfers:
1) Rinse with 1:1 nitric acid
2) Rinse with RO/DI water
3) Rinse with sample

After use:

1) Wash with detergent (Alconox or Contrad), by hand or in pipet washer, as appropriate.
2) Rinse with tap water
3) Rinse with 1:1 nitric acid
4) Rinse with RO/DI water 2X
5) Place in rack and cover

8.1.3 HNO3 Testing:

Analysis of a HNO3 blank will be analyzed with every new lot of HNO3 prior to usage. This will evaluate any possible contamination due to HNO3. Record in the HNO3 Logbook

8.1.4 Containers:

Auto Sampler Containers: Conical 15ml tubes.

8.1.5 Method Development Study (Internal Quality Control):

Before any analytical method is routinely employed, a methods development study will be undertaken to insure compliance with all published criteria. The instrument manufacturer's methods manuals and the selected analytical method source are excellent reference materials.

A.) Sensitivity checked (ABS-vs-CONC..) with mfr's published values +/- 10%.
B.) Linearity check of the concentration range of interest using 3 standards and a blank with a minimum of 3 replicate readings with the mean and standard deviation of the absorbance value calculated. Plot absorbance vs. concentration and calculate the correlation coefficient. The value should be 0.995 or better. If not, correct and repeat.
C.) Detection limits computed for each analyte according to Appendix B to Part 136,40 CFR, Revision 1.11.
D.) Accuracy checked with Certified known concentrations.
E.) Precision checked with duplicates or replicate analyses.
F.) Sample matrix interferences checked with spikes on all new matrices. Recoveries should be within those limits specified in 18th Edition Standard Methods for that analytical method (85-115%).

8.1.6 Method Detection Limit (MDL):

MDL=s must be established for all analytes, using reagent water (blank) fortified at a concentration of one to five times the estimated instrument detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined

in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

MDL = (t) x (S)

where: t = students= t value for a 99% confidence level and a standard deviation estimate with n-l degrees of freedom {t=3.14 for seven replicates].
S = Standard deviation of the replicate analyses.

Note: If additional confirmation is desired, reanalyze the seven replicate aliquots on two or more nonconsecutive days and again calculate the MDL values for each day. An average of the three MDL values for each analyte may provide for a more appropriate MDL estimate. See Attachment 8.1

MDL=s will be determined **ANNUALLY**, when a new operator begins work or whenever, in the judgement of the analyst, confirmed by the supervisor, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

8.1.7 Analyst Training:

All analysts= will be under strict supervision for the first 6 months upon learning a new instrument procedure. A training class will be provided, at the end of the 6 month training period a in-house PE sample will be issued to the analyst. Also a written exam in reference to operating procedures and chemical hygiene policies will be issued, upon completion of exam and PE the analyst will perform the duties required with limited supervision. See section 13 for complete training program. Training requirements will also apply for analysts= on rotation schedules. Refer to QA Manual Section 14.

8.1.8 Plasma Optima Standards Logbook:

All standards will be recorded in the Plasma Optima Standards Logbook. The standard book will provide a method for preparation of standards which will include the stock standard and vendor, the amount of mL's that will be used, and the total volume that will be prepared (CIVI=CFVF).

The analysts= will record the **DATE PREP**, **ANALYST INITIALS**, **LOT NO.**, **EXPIRATION DATE**, and **REFERENCE NO** in the Logbook. The reference number will correspond to the page of the specific standard-date analyzed (For example 22-031595, 22 is the page of number 031595 is the date prepared). The reference number, expiration date and analyst initials will be added to the container of the

specific standard.

8.1.9 Corrective Actions Logbook:
Each instrument will be provided with a logbook for recording all corrective actions that take place with instrument control and/or sample analysis. Samples that don't meet the acceptable criteria will also be texted, using standard language, in SQLLIMS. The logbook will also be used to document any problems that may occur prior to analysis. The purpose of this logbook is to monitor trends in

instrument and sample analysis. Texting in SQLLIMS is to provide information to our clients in reference to samples out of control.

8.1.10 Equipment Preventive Maintenance Procedure:
There are two sections to the Maintenance and Repair Logbook, section one is the Maintenance Log which will be the responsibility of the analyst, running the instrument in question, to perform the specified duties on a daily routine. A Instrument Maintenance Log Book will be maintained by the Spectroscopy Supervisor. This logbook will include all service reports generated by Perkin-Elmer. It will be the responsibility of the supervisor to order the service reports form Norwalk on a quarterly basis.

8.1.11 Performance Audits:
EPA PE and in-house PE samples will be provided to the metals quarterly by the QA Manager. Two Water Pollution Studies (WP) and two Water Supplies Studies(WS) will be performed by all analysts known to be trained and proficient in the procedure involved. Performance of EPA samples will be evaluated and reported by the suppler of the proficiency samples, all in-house proficiency samples will be evaluated by the Quality Manager at WQL. See QA Manual Section 15.

8.1.12 Internal Quality Audits:
The Quality Manager at WQL will conduct internal quality audits of the analytical procedures being performed by the staff. The internal quality audit will include observation of standard operating procedures, evaluation of the procedure for adequacy and precision, and evaluation of correct safety procedures. Proficiency samples are frequently submitted as a part of the audit process. Internal audits will be conducted yearly for all active SOP=s. See QA Manual Section 8.

8.1.13 Prioritization of Sample Type:
Due to the diversity of samples, the metals lab will employ a priority plan to run

sample types in the following order Water, Environmental Health, Urban Waters, Pretreatment, and Sludge. These procedure will help to eliminate cross contamination. RULE: RUN THE CLEANEST SAMPLE TO THE DIRTIEST.

8.1.14 Instrument Quality Control:

< Maintain a full 500 ml beaker of 1% HNO3 for aspiration when plasma is lit.

< Nebulizer Tips will be cleaned as needed to avoid cross contamination and to insure proper delivery of sample to the plasma.

8.1.15 Data Assessment Procedure for bias and precision:

A. Laboratory Performance:

< **LRB**-data is used to assess contamination from the laboratory environment. LRB values that exceed the MDL indicate laboratory or reagent contamination should be suspected. When LRB values constitute 10% or more of the analyte level determined for a sample or is 2.2 times the analyte MDL whichever is greater, fresh aliquots of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been corrected and acceptable LRB values have been obtained.

< **LCS**-Calculate accuracy as percent recovery using the following equation:

$$R = \frac{LCS-LRB}{s} \times 100$$

R =percent recovery
LCS=Laboratory Control Sample/Laboratory Fortified Blank
LRB=Laboratory Reagent (Method) Blk
s =concentration equivalent of analyte added to fortify the LRB solution

The laboratory must use LCS analyses data to assess laboratory performance against the required control limits of 85-115%. If the recovery of any analyte falls outside the required control limits of 85-115%, that analyte is judge out of control, and the source of the problem should be identified and resolved before continuing analyses.

When sufficient internal performance data become available (usually a minimum of twenty to thirty analyses), optional control limits can be developed from the mean percent recovery (x) and the standard deviation (S) of the mean percent recovery.

These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = x + 3S
LOWER CONTROL LIMIT = x + 3S

The control limits must be equal to or better than the required control limits of 85-115%. After each five to ten new recovery measurements, new control limits can e calculated using only the most recent twenty to thirty data points. Also, the standard deviation (S) data should be used to established an on-going precision statement for the level of concentrations included in the LCS. These data must be kept on file and be available for review.

< **ICVS:** When beginning the use of a method verify the calibration standards and acceptable instrument performance with the preparation and analyses of a second source standard (ICVS). If the determined concentrations are not within +/-10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before continuing with on-going analyses.

< **CCVS**: The laboratory must analyze the CCVS and a calibration blank immediately following each calibration, after every tenth sample and at the end of the sample run. Subsequent analyses of the CCVS must be within +/-10%, if it cannot be verified within specific limits, reanalyze either or both the CCVS and the calibration blank. If the second analysis of the CCVS or calibration blank confirm the calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift the instrument recalibrated. ALL SAMPLES FOLLOWING THE LAST ACCEPTABLE CCVS SOLUTION MUST BE REANALYZED.

B. Assessing Analyte Recovery and Data Quality:

< **MS/MSD:** Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Taking separate aliquot from the sample for replicate and fortified analyses can in some cases assess these effects. The analyte interference effects are operative in selected samples.

The laboratory must run a MS for every batch. In each case the MS aliquot must be a duplicate of the aliquot used for sample analysis and for total recoverable determination added prior to sample preparation. The added analyte concentration must be the same as that used in the laboratory fortified blank. Over time, samples from all routine sample source should be fortified.

Calculate the percent recovery for each analyte, corrected for concentration measured in the unfortified sample, and compare these values to the designated MS recovery range of 85-115%. RECOVERY CALCULATIONS ARE NOT REQUIRED IF THE CONCENTRATION ADDED IS LESS THAN 25% OF THE UNFORTIFIED SAMPLE CONCENTRATION. Percent recovery may be calculated using the following equation:

$$R = \frac{Cs - C}{s} \times 100$$

R = percent recovery
Cs= fortified sample concentration
C = concentration equivalent of analyte
s = concentration equivalent of analyte added to fortify the sample

If the recovery of any analyte falls outside the designated MS recovery range (but is still within the range of calibration) and the laboratory performance for that analyte is shown to be in control, the recovery problem encountered with the MS is judged to either matrix or solution related, not system related. All actions will be recorded in Corrective Action Logbook and the sample will be texted in LIMS as possible matrix interference.

8.1.16 Sample Control and Documentation:

A. Control Charts:

Two control charts will be generated for each analyte per instrument.

MEASURE ACCURACY CONTROL CHART 1:
Percent Recovery= LCS-LRB/s x100

MEASURE PRECISION CONTROL CHART 2:
Percent Difference= [LCS-LCSD]2/LCS+LCSD X100

Note: All quality control data will be documented and files will be keep in the Control Data Logbook. Disk copies of all Control Charts generated in the computer will be keep on file.

B. Corrective Actions:

All corrective actions will be documented in the Corrective Action Logbook.

8.1.17 Data Reduction/Reporting/Validation:

A. Data Reduction:

< **Instrument Criteria**: All instrument control data will be reported +/- percent difference from expected values. This will include ICVS and CCVS values.

$$\text{Calculation: } \frac{\text{Value Read - Expected Value}}{\text{Expected Value}} \times 100$$

Note: Reports will read + or - of Expected Value

< **Sample Criteria:** All sample control data will be reported as percent difference or percent recovery of absolute value.

LCS	Calculation: $\frac{\text{LCS-LRB}}{\text{s}} \times 100$	%Recovery
LCSD	Calculation: $\frac{[\text{LCS-LCSD}]2}{\text{LCS+LCSD}} \times 100$	%Difference
MS	Calculation: $\frac{\text{Cs-C}}{\text{s}} \times 100$	%Recovery
MSD	Calculation: $\frac{[\text{MS\_MSD}]2}{\text{MS+MSD}} \times 100$	%Difference

Note: MSD %Difference must be absolute value of 10% or better.
LCS %Recovery within 85-115%
MS %Recovery within 85-115%
***Control Chart LCS and LCSD

B. Reporting:

All laboratory data is entered via SQLLIMS system. Laboratory analysts are responsible for the data and result entry of the data they produce each day. All data entries will be performed at TASK LEVEL ONLY. See QA Manual Section 4.

When available the result entry using ARE will be used for instrument generated data. When this system is not available manual data entry will be used.

C. Validation: Result approval is performed at the TASK level only. A second analyst other than the analyst entering the data will verify and approve all data entry. Two signatures will be signed on all reports, the first will be the signature of the analyst who performed the test and enter the data. The second signature will be initialed by a second analyst who will validate the first analysts data.

Out of Spec Data:
A third validation will be initialed by the supervisor if QA/QC limits are out of spec. If the QA/QC requirements are not within reporting limits; data will be reviewed by supervisor. At this time samples may be re-prepped or corrective actioned. This process is to insure proper sample prep, proper entry and calculations of all data in the metals lab.

Changes In Data: Changes in data will be performed at the TASK level only. All changes in LIMS must be approved by supervisor.

8.2 Quality Control:

8.2.1 Quality Control Requirements:

The minimum requirements of this QC program consist of an initial demonstration of laboratory capability, and periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data thus generated.

***Calibration
*Calibration Curve - Blank & 3 Standards
*Calibration Verification - Blank & Standard

***Sample Analysis
*Laboratory Reagent Blank - < MDL
*Laboratory Fortified Blank - Minimum one per batch
*Laboratory Fortified Sample Matrix - Minimum one per batch
*Laboratory Fortified Matrix Duplicate Sample - Minimum one per batch

***Periodic Requirements
*EPA PE Samples - Quarterly
*Method Detection Limit - Annually
*In-house PE Samples - Quarterly

8.2.2 Instrument Performance:

Determination of linear dynamic ranges and analysis of quality control samples.

***Calibration Blank (Cal Blk)
*Acid Blank Matrix

*Auto -zero instrument
*Control Limits - Ongoing Analysis < MDL
*Frequency - Before calibration, prior to sample analysis and after every CCVS
*Corrective Action - If > MDL terminate run and correct before proceeding
*Check - 1% HNO3 contamination
*Record - Corrective actions in logbook

***Initial Calibration Standards (ICAL)

*Minimum of 3 pt calibration S1/S2/S3
* Ist source vendor - Perkin Elmer
*Control Limits - Correlation coefficient equal or greater than 0.995 for curve
*Frequency - Prior to analysis of each analyte and if CCVS criteria not meet
*Corrective Action - If criteria not meet recalibrate
*Check - Expiration date of standards, methodology applied and calculations
*Record - Corrective actions in logbook

***Initial Calibration Verification Standard (ICVS)

*Mid-range of calibration curve
*2nd source vendor - JT Baker
*Control Limits - +/- 10% expected value
*Frequency - One per each calibration curve produced
*Corrective Action - If criteria not meet rerun 2nd time, if still not corrected recalibrate

*Check -Expiration date of standard, methodology applied and calculations
*Control Chart - Verification of instrument control done for each analyte
*Record - Corrective actions in logbook

***Continuing Calibration Verification Standard (CCVS)

*Mid-range ICAL = S2
*Control Limits - Ongoing +/- 10% stated value
*Frequency - Every 10th sample and end of run
*Corrective Action - If criteria not meet rerun 2nd time, if still not corrected recal and all samples following the last acceptable CCVS must be reanalyzed
*Check - Expiration date of standard, methodology applied and calculations
*Record - Corrective actions in logbook

8.2.3 Laboratory Performance:

Determination of method detection limits.

***Laboratory Reagent (Method) Blank (LRB)**

*reagent water
*Control Limits - Analyze conc < MDL
*Frequency - Each batch of 20 or fewer samples
*Corrective Action - When LRB values constitute 10% or more of the analyte level determination for a sample or is 2.2 times the analyte MDL whichever is greater, fresh aliquot of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been corrected and acceptable LRB values have been obtained.
*Check - Laboratory or reagent contamination should be suspected
*Record - Corrective actions in logbook

***Laboratory Control Sample (LCS)**

*Control Limits - Recovery 85-115%
*Frequency - One LCS per batch
*Corrective Action - Source of the problem should be identified and resolved
*Check - Source of the problem should be identified & resolved before continuing
*Record - Corrective Actions must be recorded in laboratory logbook
*Control Chart -Verification of laboratory performance done for each analyte
*Record - Corrective actions in logbook

***Laboratory Control Sample Duplication (LCSD)**

*Analyte concentration must be the same as that used in the LCS
*Spiked sample will be carried through same analytical procedures as LCS

*Control Limits - Percent difference of +/-10% between LCS & LCSD
*Frequency - One per batch of 20 samples or less
*Corrective Action - Source of the problem should be identified & resolved
*Check - Spike solution and sample prep technique
*Record - Corrective actions in logbook

8.2.4 Data Verification:

Defines the quality of data generated.

***Laboratory Fortified Matrix (MS)**

*Analyte concentration must be the same as that used in the LFB
*Spiked sample will be carried through the same analytical procedure as samples
*Control Limits - Percent recovery for each analyte of 85-115%
*Frequency - One per batch
*Corrective Action - Source of the problem should be identified & resolved
*Check - Spike solution, methodology applied and sample prep technique
*Caution - Addition of a volume of spiking solution grater than 1-2% of the sample volume may result in significant dilution error. If the volume of the spiking solution is within 2% of the sample volume, correction for dilution is not needed.
*Record - Corrective actions in logbook

***Laboratory Fortified Matrix Duplicate (MSD)**

*Analyte concentration must be the same as that used in the LFB
*Spiked sample will be carried through same analytical procedures as MS
*Control Limits - Percent difference of +/-10% between MS & MSD
*Frequency - One per batch of 20 samples or less
*Corrective Action - Source of the problem should be identified & resolved
*Check - Spike solution and sample prep technique
*Record - Corrective actions in logbook

***Field Duplicates**

*At discretion of sampling organization

***Field Blanks**

*A field blank should be prepared and analyzed as required by the data user.

*Use the same container and acid as used in sample collection.